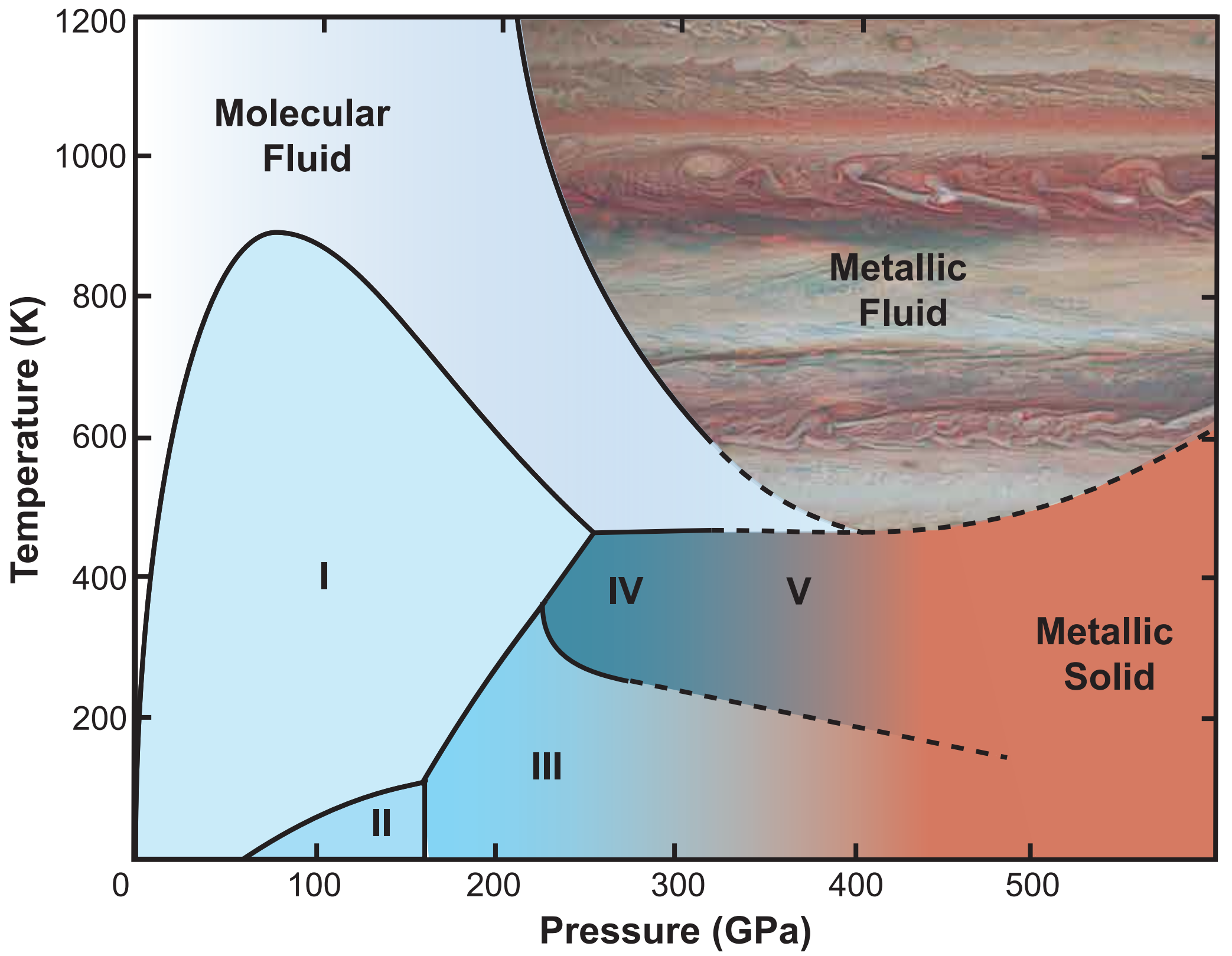
Everything You Always Wanted to Know About Metallic Hydrogen but Were Afraid to Ask


Molecular
Fluid
Metallic
Fluid
I
II
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Metallic
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Temperature (K)
Pressure (GPa)

Matter and Radiation at Extremes

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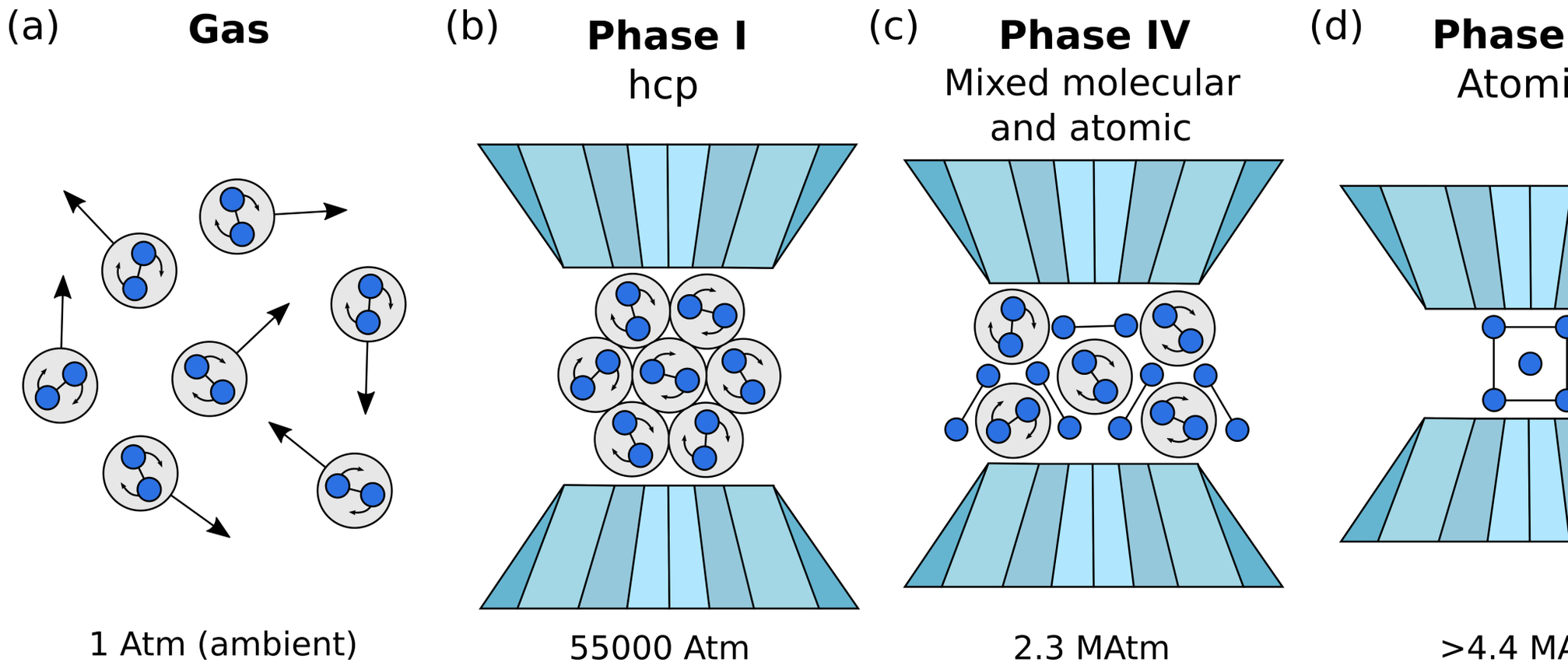

Everything You Always Wanted to Know About Metallic Hydrogen but Were Afraid to Ask

Eugene Gregoryanz[1,2,3,*], Cheng Ji[2], Philip Dalladay-Simpson[2], Bing Li[2], Ross T. Howie[2], Ho-Kwang Mao[2]
[1] *Centre for Science at Extreme Conditions and School of Physics and Astronomy, University of Edinburgh, Edinburgh EH9 3FD, United Kingdom*
[2] *Center for High Pressure Science and Technology Advanced Research, Shanghai, 201203, China and*
[3] *Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China*

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The hydrogen molecule is made from the first and lightest element in the periodic table. When hydrogen gas is either compressed or cooled it forms the simplest molecular solid. This solid possesses many interesting and fundamental physical phenomena. It is believed that if the density of the solid is increased by compressing it to very high pressures, hydrogen would transform into the lightest known metal with very unusual and fascinating properties, such as room temperature superconductivity and/or super-fluididity. In this article, we provide a critical look at the numerous claims of hydrogen metallisation and current experimental state of affairs.

1. Introduction.

In 1971, the Nobel prize winner academician Vitaly Ginzburg compiled a list of the most important and interesting questions in physics and astrophysics facing us on "the verge of XXI century" [1]. The first and second problems in the list were controlled nuclear fusion and room temperature superconductivity, whilst the third was metallic hydrogen. How the simplest element in the universe could transform to a dense metal has proven one of the most interesting and fundamental questions in condensed matter science. In the past twenty years, many of the problems Ginzburg outlined have already been solved, leading to Nobel prizes: Bose-Einstein condensates [2], discovery of the Higgs boson [3], discovery of gravitational waves [4] and the development of new types of astrophysical observations based on them. However, all evidence to date suggests we have still to reach the *solid* metallic state of hydrogen. The fact that the seemingly simple problem of hydrogen metallisation was not solved reflects the experimental difficulties associated with dealing with the material at high densities.

But why did Ginzburg place the problem of metallic hydrogen on par with Bose-Einstein condensates or room temperature superconductors? Hydrogen is the most common atom in the visible Universe. With one electron, it exists in molecular state at ambient conditions and readily forms compounds with almost every other element in the periodic table. If combined with oxygen, it forms water, the main requirement for life to exist; if combined with lanthanum it forms LaH_{10}, which to date has the highest claimed temperature of superconductivity (T_c=260 K at pressures of 180 GPa) [5]. It is thought that highly condensed metallic hydrogen is the main constituent of the Jovian planets, such as Jupiter, and is responsible for the dynamo driving the extraordinary planetary magnetic fields [6]. Here on Earth, fusion of hydrogen isotopes is widely seen as the only energy source capable of powering advanced societies over millenium timescales. Even today, hydrogen fuel cells are already being implemented on public transport systems. Being the first element of the periodic table and deceptively the simplest element, hydrogen represents a classical testing ground for many fields of science: physics, chemistry, geo- and material sciences. The current known phase diagram of hydrogen (see Fig. 1), combined with the predicted unusual properties such as superconductivity or super-fluidity, which might exist at very high compressions, make it an obvious subject to study in solid state physics and chemistry. The knowledge of its solid phases, optical properties and structures of the phases helps theory in creation of effective potentials, in testing the current theoretical models while its interaction with other elements can guide chemical physics in search for novel compounds with interesting properties.

The "metallic hydrogen problem" was actually formulated much earlier than the paper by Ginzburg in 1971 (Ref. [1] and the Nobel Lecture [7] are updated versions of the original paper written in 1971). In 1935, one of the founders of the modern solid-state physics, Eugene Wigner and his colleague Hillard Huntington first tried to predict what happened to hydrogen if it is compressed to very high densities [8]. Based on a nearly-free electron picture they predicted that above 250000 Atm or 25 GPa (unimaginable pressures at the time) hydrogen would enter a metallic state. Because they did not know the compressibility of hydrogen, they were quite far off in their estimation of pressure. Experimental high-pressure physics has developed and matured over the eight decades since, succeeding in subjecting hydrogen to pressures on the order of 400 GPa [9], almost 16-fold increase of pressures compared to the original prediction of Wigner and Huntington. The plethora of exciting and interesting phenomena happening in dense hydrogen has been observed but the metallic state still remains elusive. Due to the accumulated experience, knowledge and significantly improved experimental and theoretical methods, now we understand the problems much better and can make an educated guess which P-T conditions are needed

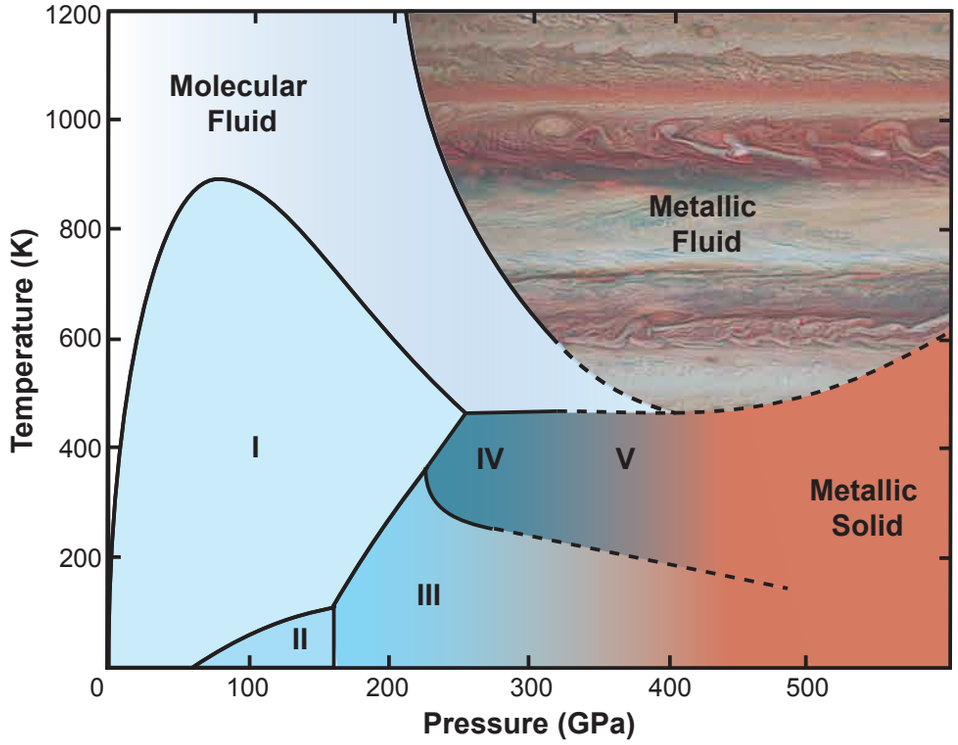

FIG. 1: Proposed *artistic P-T* phase diagram of H_2. Solid phase lines are a combination of static compression studies of solid hydrogen [9–13] and dynamic compression studies of fluid deuterium [14, 15]. Dashed lines represent extrapolations of these combined results. The dark brown colour of phases III and V at higher pressures suggests the closing band gap.

to turn molecular gas into a lightest metal. While the experimentalists are tantalisingly close to the pressures needed to metallise hydrogen, theory has already moved beyond current static pressure limits, and predicted that ground state (T=0 K) hydrogen, due to strong quantum effects, would adopt entirely new state of matter which might be super-fluid or superconducting depending on the magnetic fields applied [16]. This fascinating idea is so unusual that it is almost impossible to imagine it being real. As such, metallising hydrogen and reaching these novel states of matter could arguably be the most exciting and interesting discovery that condense matter physics can produce today.

2. Physics of dense hydrogen and deuterium at high densities (compression)

The behaviour of hydrogen is heavily influenced by quantum mechanical effects. Nuclear quantum effects are larger for hydrogen than any other atom explaining hydrogen's rather unique behaviour. Solid hydrogen has a massive quantum zero-point energy (ZPE), far greater than the latent heat of melting and has a Debye temperature well above melting. These factors determine the behaviour of hydrogen in the dense state. Currently 5 solid phases of hydrogen are known (see Fig. 1) and it is unique amongst the stable elements in that the full structural information (*i.e.* the location of the atomic centres or the shape of the molecules) is absent for all of them, which prevents the modelling and/or predictions of hydrogen behaviour at higher pressures.

At ambient conditions, *e.g.* atmospheric pressure and 300 K, hydrogen is a molecular gas (see Fig. 2(a)). The exchange interaction, a purely quantum mechanical effect, forms one of the strongest bonds in chemistry, the H-H bond. Owing to this bond, hydrogen exists in molecular form, with atoms separated by approximately 0.74 Å and a bond dissociation energy of approximately 4.52 eV at ambient condition [17, 18]. In a gas state hydrogen band gap is very large of about 14 eV [19]. Conversely, inter-molecular bonding is very weak, requiring extreme conditions to bring the molecules together and bind them into the solid state. Hydrogen was first solidified at low temperatures in 1899 by Dewar at slightly higher temperatures (19 K) then that required to liquify helium. An alternative solidification route is through compression , whereby hydrogen can be solidified at 300 K by bringing the molecules close to each other and increasing density. The gaseous, diffusive and corrosive nature of hydrogen, combined with the lack of high-pressure technologies delayed room temperature solidification by almost a century after Dewars' experiments. Only the invention and refinement of the diamond anvil cell allowed Mao and Bell to solidify hydrogen at 5.5 GPa (55000 Atm) at

300 K [20]. At these conditions the solid state is now known as phase I (Fig. 1). This phase is characterised by quantum-spherically- disordered molecules arranged in a hexagonal-close packed (*hcp*) structure (Fig. 2(b)). At room temperature and above 5.5 GPa hydrogen is a very good (molecular) insulator with the band gap of 9.5 eV (HKM, *unpublished*). Phase I occupies very prominent part of the phase diagram reaching up to 190 GPa at 300 K. Phase I displays remarkable pressure stability and to our knowledge extends over the second largest pressure range for any molecular system, being second only to molecular chlorine, whose phase I exists over a pressure interval of 230 GPa [21]. Phase II, known as the "broken symmetry" phase, is formed by compressing hydrogen (deuterium) phase I above 60 (25) GPa [13] and at temperatures below ∼100 K. Governed by the quantum effects, phase II is thought to have ordered (or at least partially ordered) molecules but the nature of their arrangement and the shape are unknown [24]. There is a strong isotope dependence in the transition from phase I to II, with the deuterium transition occurring at substantially lower pressures than in hydrogen, implying a critical role of nuclear quantum effects. Phase III is obtained by compressing phase II above ∼155 GPa below 100 K [25] or at around 190 GPa at 300 K [10, 11] (see Fig. 1). Nothing so far is known about its structure (atomic positions), but it has been shown to also have *hcp* lattice [26, 27] with unusually intense infra-red activity [28]. It was very recently shown that phase III extends over more than a 200 GPa pressure interval at low temperatures [22]. The phase diagrams of hydrogen and deuterium were studied in great detail in the 1990s leading to many interesting discoveries *e.g.* the triple point for both isotopes P-T point at which three phases I, II and III meet [29]. However, for the next 2 decades, the highest pressures hydrogen was subjected to were limited to about 300 GPa at low temperatures [30, 31] and only 160 GPa at room temperature due to the diffusive and reactive nature of the material in the dense state [32].

It had taken almost 25 years since the discovery of phase III to observe phases IV of hydrogen and deuterium [10, 33]. If phase III is compressed at 300 K, it transforms into phase IV at around 230 GPa. Phase IV is thought to be entropy driven and arguably (together with phase V, below) the most unusual phase of hydrogen. Even though the structure of phase IV is not known, on the basis of the Raman spectroscopy combined with theoretical structural searches it was speculated that it is made up of alternating layers consisting from the 6-atom rings and free-like molecules [10, 34]. The interatomic distances in the ring is around 0.82 $\AA$, leading to the significantly reduced, compared to the that at ambient conditions, vibrational frequency of around 2700 cm−1 while the atoms in the free-like molecules have vibrational frequency close to 4200 cm^{-1}. Recent x-ray diffraction study [27] demonstrated the persistence of *hcp* symmetry into phase IV despite observed fundamental changes in optical properties.

If phase IV is further compressed at 300 K it gradually transforms to phase V [9], the transformation lasting over 50-60 GPa range, starting at 275 GPa and effectively finishing at above 325 GPa . Interestingly, due to the differences in quantum mechanical properties between hydrogen and deuterium, phase V was not observed in D_2. Phase V was speculated to be a partially purely atomic state and a precursor to a fully metallic and atomic state [9].

3. Dissociation and Metallisation

Building on the earlier prediction by Wigner and Huntigton [8], Abrikosov [35] and others [36, 37], Ashcroft theorised in his seminal paper [38] that if the hydrogen molecule is dissociated and a purely atomic alkali-metal like solid is formed, this solid could exhibit room temperature superconductivity. In fact, the first experiments to break the hydrogen bond [39] were attempted by Langmuir more than 100 years ago. They demonstrated that extreme conditions are indeed needed to do so; for example, the H_2 molecule dissociates only to a minor extent at high temperatures (at 3,000 K, the degree of dissociation is around 10%) [40]. Another mechanism to break the hydrogen bond is to employ another thermodynamical variable *pressure*, exactly what Wigner and Huntington suggested some years after the Langmuir experiments. However, the proposed high-pressure route to an atomic metallic state has proved to be one of the great experimental challenges in high-pressure physics. Despite the technological advances in high-pressure physics, this theoretical prediction has yet to be experimentally confirmed. Hydrogen is expected to become metallic and also non-molecular, but the pressure at which this occurs is not known precisely; nor is it known whether metallisation and dissociation occur simultaneously. However, the recent discovery and study of phase V was the first experimental study, which suggested that the dissociation would be accompanied by metallisation and that both effects are happening simultaneously and gradually as pressure is increased [9].

The insulator to metal transition in liquid deuterium was recently claimed in the shock-wave experiments [14, 15]. However, the observed metallic liquid state of deuterium exists at relatively high temperatures (roughly around and above 1000 K [15]), which is not the ground liquid state of the system predicted theoretically. In this paper we focus only on metallic states of hydrogen (and deuterium) and their properties at "low" temperatures, namely around 300 K and below.

Shortly after hydrogen was solidified in the diamond anvil cell, it was studied by Raman spectroscopy to around 66 GPa [41]. This study found that the intramolecular vibrational frequency of hydrogen is increasing with pressure up to 33 GPa, but then it starts to decrease as more pressure is applied. Since vibrational frequency is a measure of the H-H bonding, one can easily extrapolate that at some very high pressure the bond

will be broken and molecular hydrogen could transform into an alkali-like free-electron metal *e.g.* Li or Na. The paper by Sharma *et al.*, [41] explicitly stated: *"..the increase in frequency becomes less and finally decreases at approximately 330 kbar, as the molecular bonds are weakening. Eventually when molecular hydrogen transforms to the predicted atomic (metallic) state, the molecular bonds will be broken."*

Although the sample environment of the diamond anvil cell is restricting, there are several probes, which could be used to evaluate the degree of "metallicity". However, all of these have their limitations, and combined with the hydrogen samples of 2-3 microns in linear sizes (such small sizes are required to reach pressures above 350 GPa), can easily lead to misinterpretation of the data, and in turn to erroneous claims of metallisation.

The very first claim of hydrogen metallisation happened in 1989 by a group from the Geophysical Laboratory, when on the basis of the diminishing Raman signal and increased absorption by the sample, the authors concluded that they reached the metallic state somewhere above 200 GPa [42]. This was shortly followed by another claim from a group from Harvard University [43]. However, with the development and improvement of the experimental methods it became apparent that the observed effects *e.g.* loss of Raman signal and "darkening" of the sample could be explained by loss of hydrogen at high pressures, and increased fluorescence of the diamonds mistaken for the closing band gap.

About twenty years later, there was another claim of metallisation, when combining Raman spectroscopy with direct electrical measurements of the sample resistance, a group from the Max-Planck Institute, made a bold claim to observe "liquid atomic metallic hydrogen" at above 260 GPa [33]. The claim was yet again based on the disappearance of the Raman signal and an abrupt drop of the sample resistivity at 260 GPa. Almost immediately after this paper was published, it was shown that hydrogen remains mixed molecular and atomic semiconducting solid (phase IV) to at least 315 GPa at 300 K [10] transforming to phase III at lower temperatures [11]. The loss of Raman signal and drop of the sample resistance were explained by the loss of hydrogen and the collapse of the sample chamber [44].

After the discovery of phase V above 325 GPa [9], and the suggestion that this phase could be the onset of dissociation and the first step towards a complete metallic state [9, 42], the claims of metallisation and extremely high pressures reached in the experiment started to pick up the pace (3 claims in the past 3 years). Among the many metallisation claims over the past 3 decades, the recent paper by the Harvard group arguably had been the most widely discussed due to the very outlandish statements *e.g* suggestion that metallic hydrogen produced on a pico-litter scale at 500 GPa is a good candidate for a rocket fuel [46]. Even the title of the paper "Observation of the Wigner-Huntington transition to metallic hydrogen" is misleading because the Wigner-Huntington transition is a transition between molecular and atomic state, while the paper did not demonstrate either molecular nor atomic states of hydrogen. Since the claims of metallisation and extremely high pressure of 500 GPa (which is currently widely believed to be just outside of the range of the standard diamond anvil cell techniques), were not accompanied by any any scientific evidence other than iPhone photos, 4 comments criticising the work immediately followed [47–50] and even generated "the public debate on metallic hydrogen" [51].

Currently, there is no general agreement in the high pressure hydrogen research community on the behaviour of hydrogen (and its isotopes) above 250 GPa, *e.g.* there is disagreement even on the phase diagram and the phase labelling [9, 22, 46, 52]. There is also a clear disagreement whether the metallic state was reached and at what pressures. The ultimate study will have to include robust evidence of metallisation based on techniques which directly probe the electronic state of the sample *i.e.* electrical measurements or/and reflectivity/transmission. Even if these techniques are used, one needs to make sure that the data are reliable and reproducible. For example, during the electrical measurements the electrodes will form a metallic hydride on contact with hydrogen, which could mask the real value of the resistance or due to the defusing hydrogen, the sample chamber could collapse or change shape moving and/or shortening electrodes as happened in one of the earlier measurements [33]. The reflectivity/transmission measurements are also not trivial due to the extremely small samples (2-3 micron in linear size) to which the sample collapses at around 400 GPa, changing geometry of the sample chamber which precludes proper reference measurements. The claim of metallisation at 500 GPa from the Harvard group [46] based its conclusion on 2 wavelengths points (4 different wavelengths were measured but 2 of them later retracted [53]) measured after the metallic state was supposedly reached. The lack of measurements at lower pressure, absence of raw reflectivity data and lack of any transmission data place the claim of metallisation under question.

In order to compare the results from different groups one needs to have the reliable pressure measurements. Currently, it is accepted that the pressures above 400 GPa are close to the limit of the standard diamond cell configuration technique [47–50]. The pressures are usually estimated from the shift of the Raman mode of diamond, which in turn could be cross-referenced with signal from the sample [44]. The Raman frequency of the hydrogen vibrational mode must be used to connect different experiments more reliably than the diamond shift because the state of the sample is probed directly unlike the measurements of the diamond mode shift [44]. For the infra-red reflectivity/transmission measurements the counterpart frequency could be measured and cross-referenced with the diamond shift, which would allow to compare pressures in different experiments. For instance, within the 500 GPa pressure range, Ref. [46] provided only 4 pressure measurements points using 3 dif-

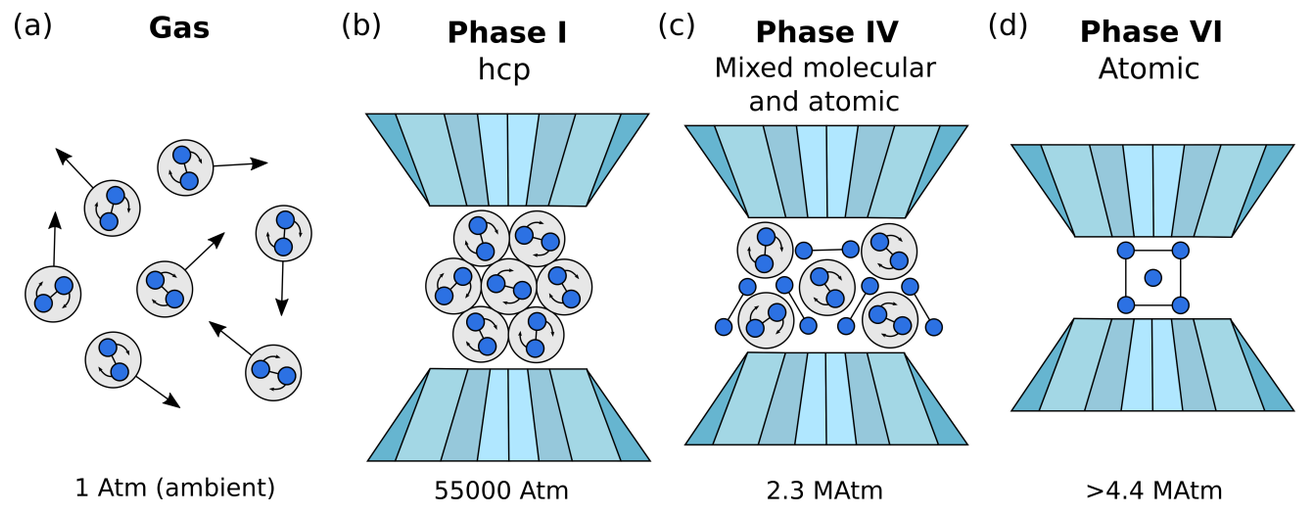

FIG. 2: Artistic representation of the gas and solid states of hydrogen at different pressures at room temperature (300 K). (a) gas molecular state (b) phase I, *hcp* structure (c) phase IV - mixed molecular and atomic state (d) purely atomic and metallic state.

ferent non-overlapping techniques extrapolating the pressure from ∼300 to 500 GPa. Not a single measurement directly related to the sample was presented. Another example of the unconvincing pressure measurements is the latest paper claiming semi-metallic hydrogen up to 480 GPa [22]. The presented diamond shift is undistinguishable from the background above 420 GPa, while the hydrogen vibrational mode disappeared at 372 GPa posing legitimate questions whether the provided pressures are correct.

The most important factor, when dealing with such a "hot" topic as hydrogen metallisation, is reproducibility. Almost all of the debunked claims of hydrogen metallisation have been based on a single unconvincing experiment, which was never later confirmed. The huge experimental research effort that is required to reach the metallic state, has resulted in researchers publishing before they can reproduce the results. Reproducibility is vital not only within ones own research group, but also with others. The "Wigner-Huntigton metallic hydrogen phase" discovery was announced more than 3 years ago [46] but the confirmation of the metallicity or any other statements made in the paper including pressures did not follow neither from the other competing groups or even more importantly from the authors themselves. The lack of reproducibility also leads to inconsistencies in the literature; the same authors who claimed the existence of the "atomic liquid metallic hydrogen" at 260 GPa in 2011 [33], recently announced semi-metallic solid hydrogen at above 400 GPa [22] leaving the readers guessing which discovery to believe. The paper's citation also creates the impression that all recent important discoveries were made by the authors [22].

Another example of the preferred interpretation of the results was presented recently in the latest claim of "a first order phase transition to metal hydrogen near 425 GPa" [54]. The authors present the infra-red absorption measurement (which by themselves are not enough to claim metallic state) demonstrating that the amount of light going through the hydrogen sample at 425 GPa compared to lower pressure is around 10^{-2}. In their earlier paper [30], where metallisation was not claimed, the same authors stated that "less than 2 x 10^{-3} of the visible white light was going through" the sample. When

the published on arXive manuscript [54] came out in Nature [55] the authors diluted the claim of metallisation by including words "*probable transition*". More interestingly, in both versions [54, 55] the claim of hydrogen being semi-metallic, as measured by directly probing the resistance of the sample [22], is swept under the carpet as "*remain unconfirmed*". It is not clear why the dubious transmission experiment is more reliable and confirming, while the direct electrical measurement, which contradicts the claim of metallicity, is not. The serious paper should include the analysis of the previous results if they happen to contradict one's claim. The excellent example of such approach is presented in Ref. [15], which analyses the discrepancy between its own results and the results of Ref. [14] obtained at essentially same P-T condition providing an alternative explanation and interpretation. Such analysis and comparison with others is only possible when other researchers' results at least are acknowledged to exist, which seems not to be the case in the static high-pressure hydrogen community.

It is clear that we are tantalisingly close to reaching the solid metallic state of hydrogen, however the reproducibility of results will require high pressure techniques to develop to the point where we can convincingly reach pressures above 400 GPa, whilst still allowing a suite of diagnostics. Only until after we can conclusively reach the solid metallic state of hydrogen can Ginzburg's third "especially important and interesting" problem in physics be struck off the list.

*e.gregoryanz@ed.ac.uk

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